

The Impact of CO₂ Clathrate Hydrate on Deep Ocean Sequestration of CO₂

Experimental Observations and Modeling Results

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ABSTRACT: CO₂ clathrate hydrate is a crystalline compound that can form under temperature and pressure conditions associated with the injection and storage of CO₂ in the deep ocean (below 500 m). At depths being considered for injection of CO₂ (between 1,000 and 1,500 m), in the absence of hydrate formation, the buoyant CO₂ would simply rise as it dissolved in the seawater. If, however, the hydrate phase forms, it will affect this process. The impact could be positive or negative, depending on how hydrate forms and whether it is associated with undissolved CO₂. This paper summarizes experimental and theoretical information relating to formation conditions for the hydrate, the relative density of the hydrate, the formation of a hydrate shell on drops of liquid CO₂, and the impact that a hydrate shell has on dissolution of CO₂. The future direction of the work is also briefly described.

INTRODUCTION

Processes for sequestering CO₂ in the deep ocean must take into account the formation of CO₂ clathrate hydrate (CO₂ · nH₂O; 6 < n < 8). Recent reports provide new insights on the ease of formation of hydrates in the deep ocean. In one case, several liters of liquid CO₂ were introduced into open containers located at 3,627 m depth in Monterey Bay.¹ Hydrate formed rapidly at the seawater/CO₂ interface and sank through the pool of liquid CO₂, which resulted in expansion of the pool beyond the confinement of the containers. In another case, Ohmura and Mori recently published an analysis of the mechanical forces associated with a hydrate film at a seawater/CO₂ interface at similar depths.² Critical conditions, beyond which such a film would not remain stable at the interface, were described. These observations and calculations show that a submerged CO₂ lake could be significantly disturbed by the formation of hydrate rather than being a quiescent pool slowly dissolving into the deep ocean.

Injection of CO₂ into the ocean at shallower depths (below 2,700 m), where CO₂ is less dense than seawater, could also be affected by the formation of hydrate. Theoretically, pure hydrate particles should sink in the ocean.³ This would facilitate sequestration by transporting CO₂ to even greater depths than used for injection.

However, our prior work has shown that various scenarios are possible at anticipated injection depths (1,000 m to 1,500 m) depending on the conditions under which hydrates are formed. In one case, hydrate structures that initially formed from a two-phase system (seawater and CO₂) floated in the seawater phase, likely due to CO₂ trapped within the hydrate particles but not incorporated into the hydrate lattice.⁴ Similar observations were made in the recent experiments in the ocean.¹ If such floating hydrates form, sequestration would be adversely impacted because the CO₂ would ultimately end up at shallower depths than planned or even in the atmosphere. On the other hand, a more dense, sinking hydrate was formed when CO₂ was first dissolved in the seawater prior to reaching hydrate-forming conditions.⁴ Another possible occurrence of hydrate is as a thin shell on CO₂ drops. At 1,000 m to 1,500 m the shells would not be thick enough to cause any but the smallest drops to sink.³ In addition, shells retard the dissolution of CO₂ into the seawater and, therefore, frustrate sequestration by allowing the hydrate-encased CO₂ drops to rise to shallower depths.⁴

Understanding hydrate formation occurrences and processes is therefore critical to successful deployment of strategies for introducing CO₂ into the deep ocean in a manner that leads to long-term storage of CO₂ in the ocean. The importance of developing models and scenarios consistent with experimental observations was recently pointed out in a review of state-of-the-art hydrate film modeling.⁵ This paper describes observations made in our laboratories concerning hydrate formation in seawater. These observations are compared to the predictions from mathematical models we have also developed.⁶ Finally, the future direction of our experimental work is briefly described.

EXPERIMENTAL

Experimental observations were made using a high-pressure, variable-volume viewcell (HVVC) of 10 cm³ to 40 cm³ capacity. The HVVC was enclosed in a chamber where the temperature could be maintained in the region of interest (0°C to 10°C). Agitation in the HVVC was provided by a glass-encased magnetic stirring bar. More complete descriptions of the HVVC and the basic procedures have been published.^{3,4} General purpose seawater, salinity of 35, was obtained from Ocean Scientific International, Ltd., Petersfield, Hampshire, U.K. SFC purity (above 99.99%) CO₂ was used.

RESULTS

Hydrate Formation from Dissolved CO₂

The bulk density of CO₂ hydrate is affected by the mode of its formation.⁴ Formation from a single-phase solution of CO₂ and seawater results in the formation of transparent, sinking hydrates. Several experiments were performed to investigate the amount of dissolved CO₂ required to form hydrate at conditions similar to those anticipated for ocean injection at approximately 1,500 m. In an experiment with an initial dissolved CO₂ concentration of 59 mg/g seawater, hydrate formed readily

with agitation at 4°C and 15.0 MPa. In contrast, in another experiment at a lower initial dissolved CO₂ level (44 mg/g seawater) hydrate did not form at similar conditions. However, hydrate was formed in this experiment when conditions were changed to simulate deeper ocean depths (2°C, 27.2 MPa). It was also noted in this experiment that at higher pressures the hydrate mass became more difficult to detect visually. At 31 MPa the hydrate mass could not be distinguished from the seawater phase. Brewer *et al.*, made the same observation in experiments at 3,650 m depth in the ocean.¹

Hydrate Shell Formation on CO₂ Drops

A model was developed in our previous work to estimate the initial and steady-state thicknesses of hydrate shells on CO₂ drops.⁶ The model assumed that the initial thickness was determined by the degree of oversaturation of the water surrounding the drop with CO₂ relative to the equilibrium saturation concentration, C_H , at the hydrate equilibrium pressure at a given temperature. The excess CO₂ could accumulate in the water during the induction period commonly observed in hydrate studies. Since the amount of dissolved CO₂ is a function of pressure, C_H would be expected to decrease with temperature in the hydrate formation region, since lower hydrate equilibrium pressures are associated with decreasing temperature. This has been observed experimentally at 30 MPa.⁷

After the initial formation, our model assumed that the thickness of the shell was governed by the rates of diffusion of the CO₂ through the hydrate shell and diffusion or convection of dissolved CO₂ away from the hydrate-covered particle. Based on these assumptions, the model predicts that the initial hydrate shell forming around drops of CO₂ injected into the deep ocean would be thin (less than 0.1 cm thick). Over time, in water unsaturated relative to hydrate forming conditions, the model also predicts that a stable hydrate shell thickness on the order of 10^{-2} to 10^{-4} times the radius of the drop will eventually result. Thus, based on this model, for drop sizes anticipated for ocean injection (up to about 1-cm radius) the initially formed hydrate shell should become thinner over time.

With the HVVC it is possible to inject drops (typically 0.5 cm to 1.0 cm diameter) of CO₂ into pressurized seawater using a high-pressure syringe pump. Such experiments have shown that drops of CO₂ only formed a hydrate shell if sufficient dissolved CO₂ is present. In the experiment described above with an initial CO₂ concentration of 44 mg/g seawater, drops of CO₂ were added and their behavior observed. The first several drops introduced into the seawater phase at 2°C, 14.5 MPa dissolved without forming a hydrate shell. Each added drop increased the dissolved CO₂ concentration. When the concentration reached 51 mg CO₂/g seawater, subsequent drops formed hydrate shells within several seconds of injection at 2°C, 17.5 MPa. An illustration of this phenomenon is shown in FIGURE 1.

FIGURE 1A shows two drops of liquid CO₂ resting at the top of the HVVC immediately prior to hydrate shell formation. FIGURE 1B shows the hydrate shell beginning to form on the lower left corner of the drop. Shell formation began at a single point and rapidly grew to completely envelop the drops, which coalesced during the process, in 1 to 2 seconds. Others have assumed that hydrate shell formation occurs uniformly across the surface of the drop, growing from hydrate clusters or

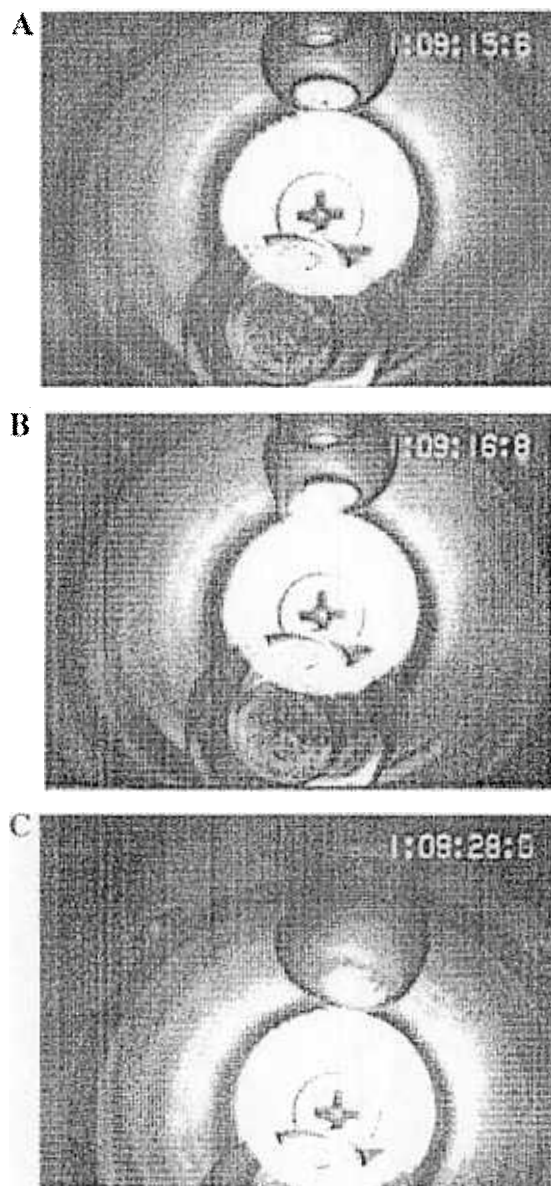


FIGURE 1. Images showing the formation of a hydrate shell on CO₂ drops in seawater. The cell is full of seawater at 2°C, 17.5 MPa. The object in the *lower part* of the images is an end-on view of a glass-encased magnetic stir bar that has a diameter of 0.01 m. In the *upper right corner* of each image is an elapsed time indication reading out to 0.1 s.

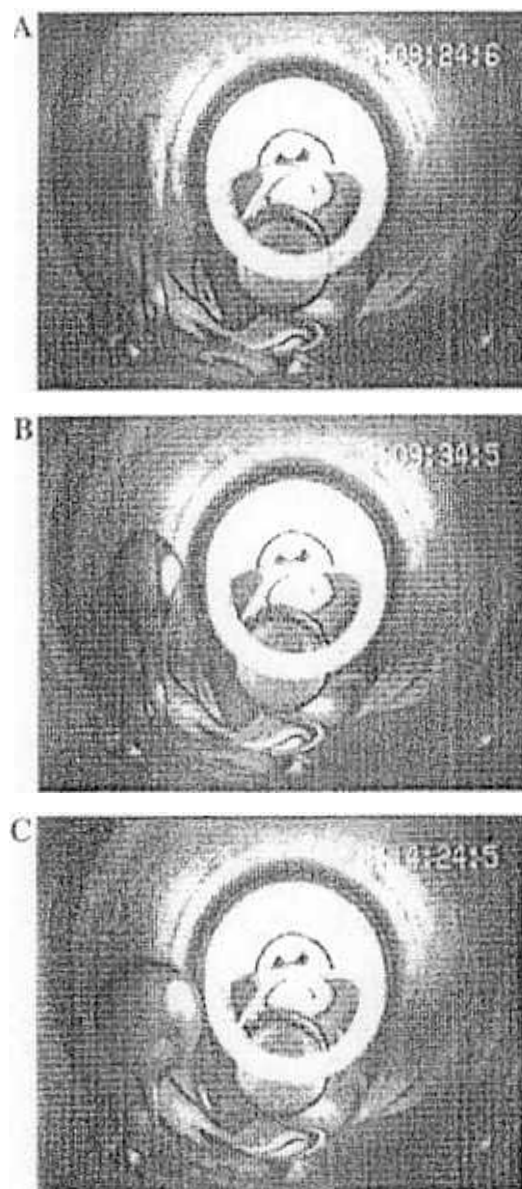


FIGURE 2. Images showing the apparent thinning of a hydrate shell. (See FIG. 1 caption for other information.)

crystallites;⁵ however, our observations on hydrate-forming systems that have just attained sufficient dissolved CO₂ do not show this to be the case. Hydrate shell formation starts at a point, usually where contact to a foreign object occurs (but not always as in FIG. 1) and then rapidly advances to envelop the entire drop. A 0.5-cm to 1.0-cm diameter drop is typically enveloped in 1 s to 2 s. FIGURE 1C shows the drop covered with a rough-textured hydrate shell. Over time the texture became smoother and the drop assumed a nearly spherical shape, indicating that the shell was thinning with time, as predicted by our model.

Another more dramatic example of a hydrate shell thinning with time after initial formation is shown in the images contained in FIGURE 2. In this experiment, the HVVC was at 2.4°C and 15.8 MPa. The dissolved CO₂ concentration was approximately 60 mg/g seawater at the time the drop was injected. The hydrate shell formed immediately and was thick enough so that its strength permitted the formation of the long tubelike structure shown in FIGURE 2A. Within seconds, however, the structure began to expand to a more spherical shape as shown in FIGURE 2B, likely due to the thinning of the shell as it approached an equilibrium thickness. FIGURE 2C shows this process has continued over a five-minute interval. This phenomenon was predicted by the modeling work summarized above.

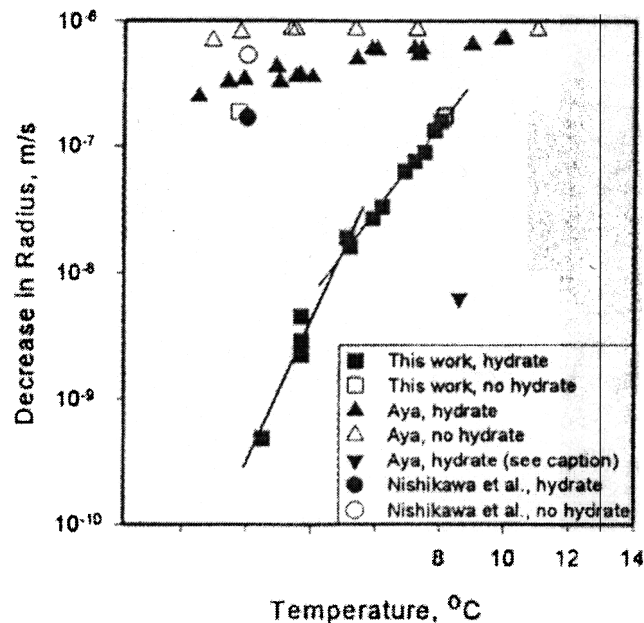


FIGURE 3. CO₂ drop dissolution data. Contains our work in seawater, Aya's work in fresh water, and the work of Nishikawa *et al.* in seawater. Aya's observation at approximately 7 wt% dissolved CO₂ is indicated by the symbol ▼.

Effect of a Hydrate Shell on CO₂ Drop Dissolution

The dissolution of CO₂ drops in water and seawater, with and without hydrate shells, expressed as the rate of radial decrease as a function of temperature, are shown in FIGURE 3. Our data were obtained during the experiment with an initial dissolved CO₂ concentration of 44 mg/g seawater. Measurements of radial shrinkage were made from recorded video images. The pressure was maintained near 17 MPa during these observations. The first several drops were injected at 1.7°C and dissolved without forming a hydrate shell. The dissolution of these drops increased the dissolved CO₂ concentration to 51 mg/g seawater. The next drops were introduced at 2°C and formed a hydrate shell within several seconds of injection. The formation of the shell caused a decline in the rate of radial shrinkage of the drops of nearly three orders in magnitude when compared to dissolution in the absence of hydrate. Additional measurements were made on the same hydrate-covered drops over a period of five days at 2.5°C to 3.7°C as they slowly dissolved. Measurements were then made over the next two days as the temperature was incrementally increased to 8.0°C, at which point these drops completely dissolved. Two final drops were then

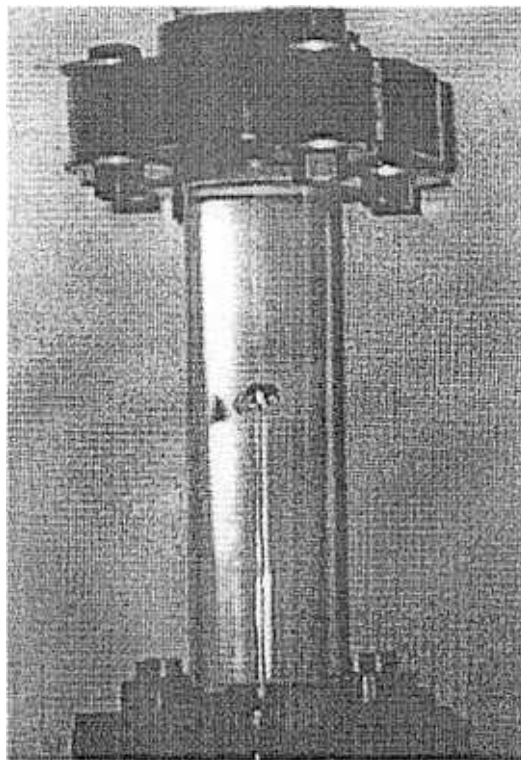


FIGURE 4. Test section of the LWTF with an air bubble stabilized in a downward flow of water.

introduced at 8.1°C that dissolved without forming a hydrate shell. The data in FIGURE 3 show that the rate of shrinkage increased with temperature, likely due to thinning of the hydrate shell that was apparent in the visual observations. The hydrate shells at the lower temperatures were rough textured for extended periods of time indicating a greater shell thickness, whereas at higher temperatures the shells became smooth. The different slopes in our data also suggest that the shells may not have thinned to a steady state thickness during the observation periods at the lower temperatures.

Data from other researchers are also shown in FIGURE 3. The data of Aya were obtained in a 32 L vessel at 30 MPa in fresh water.⁸ Nishikawa *et al.*, obtained their data in a 16.7 L vessel at 30 MPa in artificial seawater recirculated at different flow rates.⁹ The two data points of Nishikawa *et al.* shown in FIGURE 3 were obtained by extrapolation to zero flow. Neither investigator mentions dissolved CO₂ content, except that Aya notes one observation in water with about 7 wt% CO₂.

Previous investigators did not always indicate the levels, if any, of dissolved CO₂ present in their studies. Based on the results reported here, this information should be provided by investigators in future. The data in FIGURE 3 show dramatic differences, not only in the rates of radial decrease, but also in the relative differences

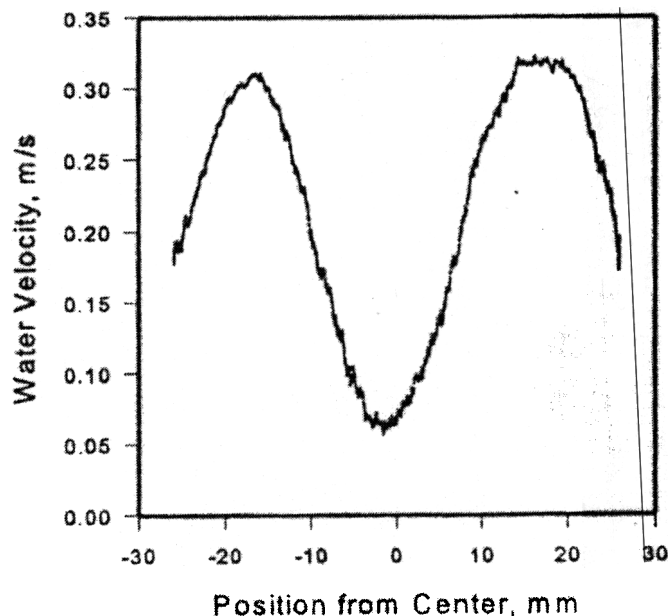


FIGURE 5. Example of the measured velocity profile across the viewing section of the LWTF. The measurements were made with an S-type pitot tube constructed of 1/16" dia stainless steel tubing and housed within a 3/16" tube. The pitot tube was translated across the bore using a stepper motor under control of a computer which also collected 5,000 data points during the transverse. Calibration of the probe was achieved by timed positive displacement measurements.

between drops with and without hydrate, especially at the lower temperatures. The different pressures, drop sizes, and vessel configurations undoubtedly are involved. Our vessel had a much smaller volume than the others, which would permit dissolved CO_2 levels to more rapidly equilibrate.

Development of a Water Tunnel Facility

To more accurately simulate CO_2 in the oceanic water column, a high-pressure water tunnel facility is being built in our laboratory. The device will permit stabilization of rising or sinking CO_2 drops in a visual observation area for extended periods of time using a countercurrent flow of water or seawater following design principles established in the literature.^{10,11} In this device, as in the ocean, a drop will not touch a containment structure but will encounter only the fluid phase while being subjected to changing conditions of temperature, pressure, and dissolved CO_2 content, giving a more accurate simulation of the drop's journey in the ocean water column.

A low-pressure water tunnel facility (LWTF) has been constructed for the purpose of refining design geometries of the viewing section and flow conditioning elements, to permit stabilization of the drop in both the radial and axial directions. In initial experiments, air bubbles and plastic spheres of varying density were successfully stabilized in a countercurrent flow of water. FIGURE 4 shows an air bubble that has been stabilized in the LWTF. Such bubbles have been stabilized and observed for several hours. FIGURE 5 shows an example of the velocity profile measured across the center of the viewing section. The velocity minimum in the center of the viewing section provides for radial stabilization of the object. Further refinements in the design are being made to optimize stabilization at the slower flow rates needed for objects that would have densities closer to that of compressed liquid CO_2 .

REFERENCES

1. BREWER, P.G., G. FRIEDERICH, E.T. PELTZER & F.M. ORR, JR. 1999. *Science* 284: 943-945.
2. OHMURA, R. & Y.H. MORI. 1998. *Environ. Sci. Technol.* 32: 1120-1127.
3. HOLDER, G.D., A.V. CUGINI & R.P. WARZINSKI. 1995. *Environ. Sci. Tech.* 29: 276-278.
4. WARZINSKI, R.P. & G.D. HOLDER. 1997. *In Proceedings of the 9th International Conference on Coal Science 1879-1882.*
5. MORI, Y.H. 1998. *Energy Convers. Mgmt.* 39: 1537-1557.
6. HOLDER, G.D. & R.P. WARZINSKI. 1996. *In Preprints of Papers, American Chemical Society, Division of Fuel Chemistry.* 41: 1452-1457.
7. AYA, I., K. YAMANE & H. NARIAL. 1997. *Energy (Oxford)* 22: 263-271.
8. AYA, I. 1995. *In Direct Ocean Disposal of Carbon Dioxide.* N. Handa & T. Ohsumi, Eds.: 233-238. Terra Scientific Publishing Co., Tokyo.
9. NISHIKAWA, N., M. ISHIBASHI, H. OHTA, N. AKUTSU, M. TAJIKA, T. SUGITANI, R. HIRAKAWA, H. KIMURO & T. SHIOTA. 1995. *Energy Convers. Mgmt.* 36: 489-492.
10. MAINI, B.B. & P.R. BISHNOI. 1981. *Chem. Eng. Sci.* 36: 183-189.
11. MOO-YOUNG, M., G. PULFORD & I. CHEYNE. 1971. *Ind. Eng. Chem. Fundam.* 10: 157-160.